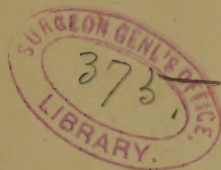
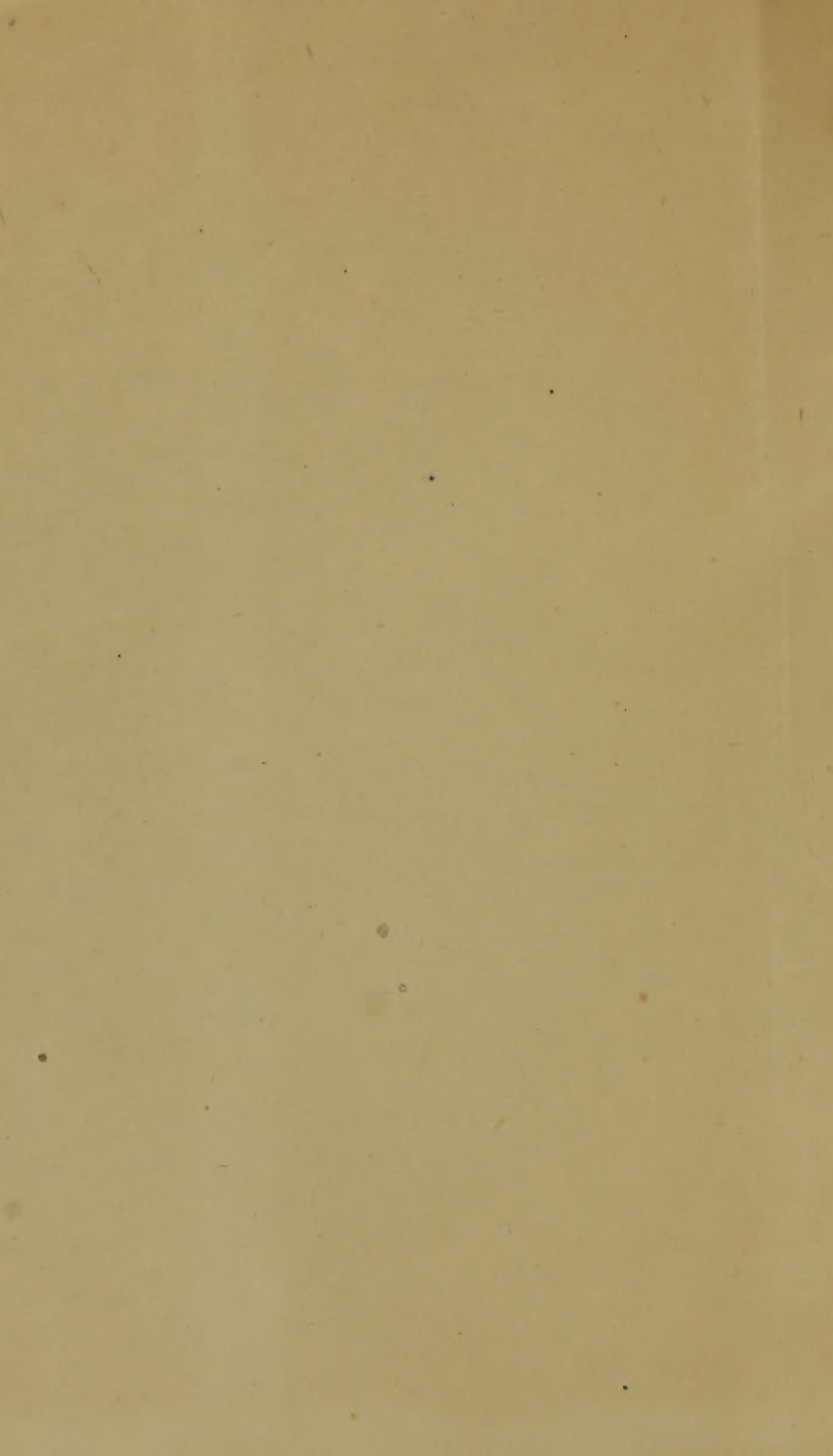


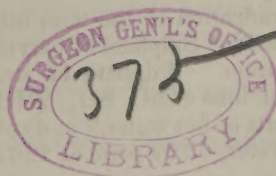
HORSFORD (E.N.)

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Connection between the Atomic weights and the physical and chemical properties of Barium, Strontium, Calcium and Magnesium, and some of their Compounds; by E. N. HORSFORD, Rumford Professor in the University at Cambridge.

Read before the Cambridge Scientific Association.*

THE great discovery of isomorphism by Mitscherlich,† and the affiliated one by Kopp,‡ of the identity of the specific volumes of isomorphous bodies are among the brilliant points in the progress of the chemistry of this century.

The latter seems to have had its origin in a conviction that in the atomic weight of a body—all its attributes have what may be denominated a *product expression*. The factors are *form*, *volume* and *density*. Each may vary, and with it the atomic weight will vary; for example:—the volume and form being constant, increase of density will be accompanied by increase of atomic weight: or form being constant, increase of density will be accompanied by increase of atomic weight, or, density and volume being constant, modification of form will influence the atomic weight.

The object of the following paper is to show that the properties of the metals, barium, strontium, calcium and magnesium, and of their compounds generally, are, in their intensity, in the order of their atomic weights. It will be seen that the law is more true of the first three than of these taken in connection with the fourth.§

The signification of the term intensity, as used above, may be thus illustrated. Sulphate of baryta requires 43000 parts of water for its solution. Sulphate of strontia 15029 parts at 11° C.|| Sulphate of lime ($\text{CaO}, \text{SO}_3, 2\text{HO}$) in 380 parts of cold water, and 388 parts of hot water,¶ and sulphate of magnesia with seven atoms of water, 0.799 parts at 18.75°.**

	Solubility.	At. W.
BaO, SO_3	43000.00	116.5
SrO, SO_3	15029.00	91.7
CaO, SO_3	460.00	68.
MgO, SO_3	0.79	60.7

* A summary of some of the conclusions arrived at by the author were communicated to the American Association of Geologists and Naturalists, at their meeting in Boston in 1849.

† Ann. Chim. Phys., xiv, 172; xix, 350; xxiv, 264, 265. Pogg. Ann., xii, 137; xxv, 300; xlix, 401.

‡ Pogg. Ann., xlvii, 132; lii, 243–262. Ann. Chem. u. Phar., xxxvi, 1.

§ It is to be regretted that so little is known of the properties of the compounds of magnesia. Their eminent solubility in water, and the difficulty with which any of the salts of this base may be made to crystallize, have made this field of investigation less inviting than many others.

|| Brandes u. Silber, Br. Arch., xxxiii, 61.

¶ Giese. According to Bucholz, 480 parts cold or hot.

** Gay Lussac. The anhydrous sulphate is soluble at 0° C. in 3.885 parts of water.

Here *intensity* is the same as *degree of solubility*. In other words, the solubilities of the above salts are in the order of their atomic weights.

The truth of the general proposition will be apparent from considering the following facts.

I. Barium unites with two atoms of oxygen, and is stable in this state of combination at ordinary temperatures.*

Strontium and calcium peroxyds are only known in combination with water.†

Magnesium combined with two atoms of oxygen is unknown.

II. Barium, strontium and calcium all oxydate at ordinary temperatures in the air.

Magnesium does not.

III. Barium thrown into water causes decomposition with a stormy evolution of hydrogen gas.

Strontium and calcium are both dissolved with escape of hydrogen.

Magnesium may be washed in water that has been thoroughly freed from air by boiling, without diminution of its lustre.

IV. Baryta moistened with water enters into combination with it, attended by such evolution of heat as melts the hydrate formed.‡

Strontia falls with water to a white pulverulent hydrate, with the production of intense heat. Lime similarly treated yields a heat that will fire sulphur.§

Magnesia in uniting with water is but slightly heated.||

V. Hydrate of baryta loses none of its water under intense red heat.¶

Hydrate of strontia, by long continued red heat, melts, and by higher heat loses all its water.**

Hydrate of lime, by moderate red heat without melting, loses its water.

Hydrate of magnesia loses its water below the red heat.

VI. Carbonate of baryta, an hour and a half exposed to the most effective blast furnace heat, loses its carbonic acid.††

Carbonate of strontia, loses its carbonic acid in the strong heat of an open fire.‡‡

Carbonate of lime is decomposed at a red heat.

Carbonate of magnesia loses its carbonic acid at a moderate red heat.

VII. Selenite of baryta and selenite of strontia are insoluble in water.

* Thenard. Ann. Chem. Phys., viii, 308. Rammelsberg, Pogg., xlv, 558.

† Thenard. Ann. Chem. Phys., viii, 313.

‡ Döbereiner. Schw., vi, 367.

§ Ann. Chem. Phys., xxiii, 217.

|| H. Davy.

¶ Bucholz u. Gehlen, iv, 258.

** Denham Smith. Phil. Mag., ix, 87. Pogg., xxxix, 196.

†† Abich, Pogg., xiii, 314.

‡‡ Ibid, 315.

Selenite of lime and selenite of magnesia are slightly soluble in water.

VIII. Biselenite of baryta dissolves with difficulty in water.

The same is true of the corresponding salts of strontia and lime.

Biselenite of magnesia is a doughy deliquescent uncrystallizable salt.

IX. Selenate of baryta is as little soluble as the sulphate.*

Selenate of magnesia is equal in solubility to the sulphate.†

X. Iodid of barium crystallized with an atom of water, is readily soluble in water, but does not deliquesce upon exposure to the air.‡ It is deliquescent.§ It is not fusible.

Iodid of strontium is readily soluble in water.|| It is fusible below red heat.

Hydrated iodid of calcium may be crystallized. It deliquesces on exposure to the air,¶ and fuses below red heat.

Hydrated iodid of magnesium crystallizes with difficulty, and deliquesces readily.

All decompose, when heated by access of air, into metallic oxyds.

XI. Iodate of baryta with one atom of water is soluble in 1746 parts of water at 15° C. and in 600 of boiling water.**

Iodate of strontia with six atoms of water is soluble in 342 parts of water at 15° and in 110 of boiling water.††

Iodate of lime with five atoms of water dissolves in 253 parts of water at 15° C. and in one hundred and ten parts of boiling water.‡‡

Iodate of magnesia is soluble in water, but has not been further examined.

XII. Bromid of barium with two atoms of water is unaffected by exposure to air.

Bromid of strontium with six atoms of water loses its water at a feeble heat.§§

Anhydrous bromid of calcium deliquesces rapidly in the air. That with one atom of water crystallizes with difficulty from the solution of bromid of calcium.

XIII. Bromates of baryta, strontia, lime and magnesia crystallize with water, the first three with a single atom.

Bromate of baryta loses its atom of water not below 200° C.

Bromate of strontia by 120° C., bromate of lime by 180° C. and bromate of magnesia at ordinary temperatures.

XIV. Bromate of baryta dissolves in 130 parts of cold water.

* Berz. Pogg., xxxii, 11.

† Gay Lussac.

‡ Berthemot. J. Pharm., xiii, 416.

** Rammelsberg.

§ O. Henry.

†† Ibid.

‡ Berz. Schw., xxiii, 454.

|| Gay Lussac.

¶ Ibid.

§§ Löwig.

Bromate of strontia in three parts; bromate of lime in 1.1 parts, and bromate of magnesia in 1.4 parts.*

XV. When chlorid of barium is formed by leading the vapor of hydrochloric acid over heated baryta, the decomposition is attended with the evolution of heat and a red light. The same phenomena occur in the similar production of chlorid of strontium.

That of chlorid of calcium is attended with heat only.

Chlorid of magnesium cannot be formed in this manner.

XVI. The specific gravity of anhydrous chlorid of barium is 3.7037, of chlorid of strontium 2.8033, of chlorid of calcium 2.0401.†

XVII. When heated in dry air, chlorids of barium, strontium and calcium become alkaline; while chlorid of magnesium remains unchanged.

XVIII. Crystallized chlorids of barium and strontium do not change upon exposure to the air.

The chlorids of calcium and magnesium deliquesce rapidly upon exposure to the air.

XIX. Chlorid of barium is soluble in from 8108–6885 parts of cold alcohol, of 99.3 per ct., and in 4875 parts of boiling alcohol.

Chlorid of strontium is soluble in from 116.4–111.6 parts of cold and in 262 parts of boiling alcohol of 99.3 per ct.‡

XX. Chlorate of baryta requires four parts of water for its solution.

Chlorates of strontia, lime and magnesia deliquesce in the air.

XXI. Chlorate of baryta is insoluble in alcohol.

Chlorates of strontia, lime and magnesia are soluble in alcohol.

XXII. Fluorid of barium is readily soluble in hydrochloric and nitric acids.

Fluorid of calcium is slightly soluble in boiling acids, and fluorid of magnesium scarcely at all in cold or hot acids.

XXIII. Fluorid of barium is soluble in aqueous hydrofluoric acid; fluorid of strontium less; fluorid of calcium a mere trace, and fluorid of magnesium not at all.

XXIV. Nitrites of baryta and strontia do not change in air.

Nitrites of lime and magnesia deliquesce upon exposure to the air.§

XXV. Nitrate of baryta requires 20 parts of water at 0° for solution. Nitrate of strontia 5 parts of cold water. Nitrates of lime and magnesia deliquesce most rapidly in the air.

XXVI. Nitrates of baryta and strontia are not soluble in alcohol. Nitrates of lime and magnesia are soluble.

* Rammelsberg. Pogg. Ann., lii, 81.

† Fresenius. Liebig's Ann., Bd. lix. 117–128.

‡ Karsten.

§ Mitscherlich.

XXVII. Carbonate of baryta is soluble in 14137 parts of cold, in 15421 of boiling water. Carbonate of strontia in 18045 parts cold water. Carbonate of lime in 10601 of cold and 8834 of boiling water.*

XXVIII. Oxalate of baryta with one atom of water is soluble in 200 parts of cold or boiling water.†

Oxalate of strontia with one atom of water is insoluble in water‡—even in boiling water.§

Oxalate of magnesia with two atoms of water only very slightly soluble in water.||

XXIX. Formiate of baryta is soluble in 4 parts of cold water.¶

Formiate of lime in 8 parts of cold and in 10 parts at 19° C.**

Formiate of magnesia is soluble in 13 parts of cold water.††

XXX. Sulphovinate of baryta is soluble in 0.92 parts of water at 17° C.‡‡

Sulphovinate of lime is soluble in 0.8 parts of water at 17° C.§§

XXXI. Acid urate of baryta is insoluble in water. That of strontia somewhat soluble in hot water. That of lime of difficult solubility. That of magnesia, is soluble in 3500–4000 parts of cold and 150–170 parts of boiling water.||||

XXXII. Neutral alloxanate of baryta is less soluble than the corresponding salts of lime and magnesia.

XXXIII. The above salts of lime and magnesia are somewhat soluble in alcohol. The salt of baryta is not.¶¶

XXXIV. Ferrocyanid of barium ($\text{Ba}_2\text{Fe Cy}_3$) dissolves in 584 parts cold,*** 1800,††† and in 116 parts of boiling water.‡‡‡

Ferrocyanid of strontium dissolves in 2 parts of cold and 1 of boiling water.§§§

Ferrocyanid of calcium deliquesces in the air.|||||

Ferrocyanid of magnesium with 12 atoms of water dissolves in 3 parts of water.¶¶¶

It is to be regretted that other properties, including specific gravity, specific heat and light-refracting and heat-conducting power have been so little studied. Still, enough of correspondence and gradation among the properties of the compounds of this group has been shown to establish the general proposition that the intensities of their chemical attributes are in the order of the atomic weights of the metals, and lead to the conviction that other attributes might be found to be in similar gradation of intensity.

* Fresenius. Liebig's Ann., Bd. lix, s. 117–128.

† Bucholz. Taschenbuch, 18. 18.

‡ Scheele.

§ Wackenroder.

|| Graham. ¶ Arvidson.

** Gobel.

†† Arvidson.

‡‡ Magnus.

§§ Marchand.

|||| Bensch.

Liebig's Ann., liv, 189–208.

¶¶ Schlieper, Liebig's Ann., Bd. lv, s. 272–279.

*** Duflos.

††† Porret.

‡‡‡ Duflos.

§§§ Bette. Ann. Pharm., xxviii, s. 54.

|||| Ittner.

¶¶¶ Bette. Ann. Pharm., xxii, s. 152; xxiii, s. 115.

The resistance to the passage of an electric current through the fluid solutions of these bodies might, it was conceived, be in the order of their atomic weights.

To ascertain if this supposition were founded, an apparatus was employed an account of which has been published in my paper upon the resistance of fluids to electric conduction,* and may be referred to here, as a perusal of this description will be necessary in order to the appreciation of the application of the law.

The fluids employed were nitrates, hydrochlorates and acetates of baryta, strontia, lime and magnesia.

The baryta and strontia salts were prepared from the sulphids (derived from the native sulphates by reduction with charcoal and rye meal); the lime salts from the hydrate, and the magnesia salts from magnesia alba.

The barium and strontium sulphids were dissolved in the several acids with slight excess of acid filtered, neutralized by addition of hydrates of baryta and strontia to the respective solutions, concentrated by evaporation, crystallized, and the crystals washed and dissolved.

The hydrate of lime was dissolved in the several acids, the solutions kept alkaline by excess of lime to precipitate the iron, filtered, and accurately neutralized.

The magnesia alba, with the aid of heat, was dissolved in the several acids and carefully neutralized.

A saturated solution of chlorid of barium, the least soluble of the salts employed, at 16° C., had a specific gravity of 1.042. The solutions of the other chlorids and remaining salts were with great care brought to the same degree of dilution. Two series of results were obtained with the solutions of chlorid of barium and chlorid of strontium. The series in column I. were with solutions of the specific gravity above mentioned. The series in column II. with these solutions diluted with equal measures of distilled water, presenting in an equal length and breadth of liquid, twice the depth. It will be seen that the resistance was very nearly the same.

The solutions of 1.042 specific gravity were then successively placed within the galvanic circuit, and a constant length, breadth and depth of the liquid maintained, and the obstruction they presented to the electric current replaced by windings of German silver wire. The windings correspond to and express the resistance the liquids severally presented.

Table I. presents the results obtained under the following conditions.

* Pogg. Ann., Bd. lxx, s. 238, and Amer. J. Sci., vol. v, ii ser., 1848, 343.

Specific gravity of liquid, 1.042
 Cross section of liquid, 0.00172 M.
 Length of layer, 0.4 M.
 Strength of battery, 5 Bunsen's pairs.

The exceptions in relation to the results under II. and III. have already been alluded to.

Column A contains the number of experiments; column B, the degrees of deflection of the magnetic needle as indicated by the galvanometer; column C, the windings and decimal fractions of windings of German silver wire, as indicated by Wheatstone's Regulator.

TABLE I.

		BaO, HCl		BaO, HCl		SrO, HCl		SrO, HCl		CaO, HCl		MgO, HCl	
		I.		II.		I		II.					
A	B	C	B	C	B	C	B	C	B	C	B	C	
1	14°	37.42	14°	36.04	14°	24.07	15°	28.68	16°13'	22.98	16°15'	23.18	
2	11	39.60	12	38.10	13	27.91	12	27.04	15	22.90	19	21.87	
3	12	35.50	15	26.62	12	26.78	15 30	22.95	16	22.80	
4	13	34.00	13	26.88	15 30	23.84	14	23.71	
5		12	27.34	14	21.75	22.89	
Average,		36.63	..	37.07	..	26.56	..	27.50	22.88	22.89	

The subsequent experiments were made with the platinum diaphragms .25 M asunder, the specific gravity 1.042 and the remaining conditions the same as in the experiments above recorded.

It will be observed that the resistance is pretty nearly in the ratio of the diminished length of the layer of liquid in the case of the hydrochlorates. The want of precise correspondence was ascribed to the presence of chlorine upon the platinum plates producing the effect of so-called polarization. The odor of chlorine was remarked in the experiments with the hydrochlorates.

TABLE II.

No. of experiment.	Deflection of needle.	BaO, HCl		SrO, HCl	Deflection of needle.	CaO, HCl		MgO, HCl
		Windings of German silver wire.	Deflection of needle.			Windings of German silver wire.	Deflection of needle.	
1	13°	20.36	12°	17.09	16°	15.12	18°	14.90
2	"	20.73	14	17.38	"	15.19	"	14.60
3	"	21.93	14 30'	17.36	"	15.15	"	14.92
4	"	20.45	"	17.81	"	14.70	"	14.72
5	"	20.98	14	17.97	"	15.10	"	14.45
6	"	21.75	"	17.89	"	15.30	"	14.49
7	"	20.75	"	17.65	"	14.54	"	14.99
8	"	20.28	"	17.70	"	15.03	"	13.90
9	"	20.04	"	16.93	"	"	"	14.05
10	"	20.18	"	17.00	"	"	"	14.14
11	"	20.94	"	17.03	"	"	"	14.94
12								14.88
Average		20.76		17.34		15.01		14.54

TABLE III.

No. of experiment.	Deflection of needle.	BaO NO ₅ Windings of German silver wire.	Deflection of needle.	SrO, NO ₅ Windings of German silver wire.	Deflection of needle.	CaO, NO ₅ Windings of German silver wire.	Deflection of needle.	MgO, NO ₅ Windings of German silver wire.
1	14°	31·25	14°	29·31	17°	20·29	16°	17·66
2	"	31·15	"	29·47	16	21·41	"	17·97
3	"	30·25	"	29·26	"	20·47	"	17·90
4	"	31·78	"	28·90	"	21·10	"	17·34
5	"	30·00	"	29·10	15	21·39	"	17·99
6	"	31·20	"	28·76	"	20·81	"	17·72
7	"	30·23	"	28·50	"	20·02	"	17·28
8	"	30·07	"	28·12	"	21·57	"	17·85
9	"	30·37	"	29·22	"	20·45	"	17·01
10	"	30·00	"	28·40	"	20·20	"	17·90
11	"	30·08	"		"	20·10	"	17·21
					"	20·00	"	17·62
					"	20·01	"	17·57
					"	20·15		
					"	20·58		
Average		30·58		28·90		20·57		17·62

TABLE IV.

No. of experiment.	Deflection of needle.	*BaO, A Windings of German silver wire.	Deflection of needle.	SrO, A Windings of German silver wire.	Deflection of needle.	CaO, A Windings of German silver wire.	Deflection of needle.	MgO, A Windings of German silver wire.
1	9°·30'	34·48	12°	36·33	12°·30'	36·42	12°	35·26
2	"	34·02	"	36·00	11	36·12	"	34·60
3	"	34·00	12°·30'	36·97	9°·30	36·62	"	35·08
4	"	34·50	"	36·00	9	35·00	"	35·29
5	"	34·90	"	36·55	8°·30	35·31	"	35·69
6	"	34·26	"	37·39	"	35·00	"	35·45
7			"	36·13	"	35·25	"	35·04
8			"	37·25	"	35·39	"	35·09
9			"	36·27	"	35·60		
10			"	37·02				
11			"	37·00				
12			"	36·03				
13			"	36·04				
14			"	37·15				
Average		†42·95		36·50		35·63		35·18

SUMMARY OF RESULTS.

I.

Salts.	Atomic weights.	I.	Results.	II.	III.
BaO, HCl,	152·0	36·63	37·07	20·76	
SrO, HCl,	88·3	26·56	27·50	17·34	
CaO, HCl,	64·5	22·88	.	15·01	
MgO, HCl,	56·7	22·89	.	14·54	

II.

BaO, NO ₅ ,	.	.	130·5	30·58
SrO, NO ₅ ,	.	.	105·8	28·90
CaO, NO ₅ ,	.	.	82·0	20·57
MgO, NO ₅ ,	.	.	74·2	17·62

* Length of liquid section ·20 M.

† ·20 gave 34·36, ·25 would give 42·95.

III.

BaO, \bar{A} ,	127.5	42.95
SrO, \bar{A} ,	102.8	36.50
CaO, \bar{A} ,	79.0	35.63
MgO, \bar{A} ,	71.2	35.18

The above results led to the conviction that all the attributes of these metallic bases and their compounds would probably be found intense in the order of their atomic weights, a conviction which I expressed after presenting a summary of the foregoing results, to the meeting of the American Association in 1847.

I had then projected the scheme of decomposing the several salts of these bases by transmitting steam over them while subjected to heat. Circumstances prevented my realizing this intention, and in the following year, Mr. Tilghman of Philadelphia, to whom my researches could not have been known, as they had not been published, announced the results of a series of most important experiments—under the head of “Decomposing power of water at high temperatures.”*

Mr. Tilghman found that, while a moderate heat was required to decompose sulphate of magnesia with the aid of steam, a higher one was necessary for sulphate of lime, a still higher one for sulphate of strontia, and the highest of all for sulphate of baryta. Thus, their susceptibility to decomposition is in the order of their solubility, viz.—

1. MgO, SO ₃		3. SrO, SO ₃
2. CaO, SO ₃		4. BaO, SO ₃

This research fulfilled my expectations, and it would seem that there can be little hazard in considering the above facts as illustrations of a natural law applying to the group of the alkaline earths.

* Chem. Gaz., 1848, p. 181.

